PREPARATION AND CHARACTERIZATION OF CATALYST FROM LOCAL INDUSTRY WASTE, RED GYPSUM FOR BIODIESEL SYNTHESIS

VELA A/L LAI KIN MING

UNIVERSITI MALAYSIA PAHANG

PREPARATION AND CHARACTERIZATION OF CATALYST FROM LOCAL INDUSTRY WASTE, RED GYPSUM FOR BIODIESEL SYNTHESIS

VELA A/L LAI KIN MING

A thesis submitted in fulfillment of the requirements for the award
of the degree of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

PREPARATION AND CHARACTERIZATION OF CATALYST FROM LOCAL INDUSTRY WASTE, RED GYPSUM FOR BIODIESEL SYNTHESIS

ABSTRACT

Red gypsum, a reddish brown semi-solid mud is a waste product of local industry in Malaysia which is formed during the extraction of titanium (IV) oxide from the ilmenite ores and they are accumulating in landfill and polluting the environment.The total accumulation of red gypsum in Malaysia is at least 340,000 tons per year. This research is done to find an end use for red gypsum waste that has been land filling and polluting the environment. At the same time there is a crucial need to find an alternative fuel in fulfilling energy demand to replace fossil fuels which are undergoing drastic depletion. The best option is biodiesel which shows almost same properties like fossil fuels and most importantly it is environmental friendly. The major composition of red gypsum are CaSO4.2H2O (70 wt %), Fe2O3 (30 wt %) and small amount of Al2O3 is a potential source for catalyst production which later can be used as solid base catalysts in biodiesel production. The objectives of this research are to produce and characterize catalyst from waste red gypsum and study the activity of catalyst for esterification of FFA. Preparation of catalyst from red gypsum through heat treatment in furnace using activated carbon as reducing agent was investigated in this work. Characterization of the catalyst produced is done using X-Ray Diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and Field Emission Scanning Electron Microscopy (FESEM). The performance of the activity of the catalyst produced is studied by esterification of oleic acid with ethanol in a 1:6 molar ratio. Different amount of catalyst is used ; 5%,3% and 1% weight catalyst of oleic acid to find the free fatty acid, FFA conversion and the catalyst activity is studied based on the result obtained.

PENYEDIAAN DAN PENCIRIAN PEMANGKIN DARI SISA INDUSTRI TEMPATAN, GIPSUM MERAH UNTUK SINTESIS BIODIESEL

ABSTRAK

Gipsum merah, lumpur separa pepejal bewarna merah, adalah produk sisa industri tempatan di Malaysia yang terbentuk semasa pengekstrakan oksida titanium (IV) dari bijih ilmenit dan mereka terkumpul di tapak pelupusan dan mencemarkan persekitaran.Jumlah pengumpulan gipsum merah di Malaysia adalah sekurang-kurangnya 340,000 tan setahun. Kajian ini dilakukan untuk mencari penggunaan akhir bagi sisa gipsum merah yang telah mengisi tanah dan mencemarkan alam sekitar. Pada masa yang sama, terdapat keperluan penting untuk mencari bahan api alternatif dalam memenuhi permintaan tenaga untuk menggantikan bahan api fosil yang sedang menjalani pengurangan drastik. Pilihan yang terbaik adalah biodiesel yang menunjukkan ciri-ciri yang hampir sama seperti bahan api fosil dan yang paling penting ia adalah mesra alam. Komposisi utama gipsum merah ialah CaSO4.2H2O (70% berat), Fe2O3 (30% berat) dan sedikit Al2O3 dan ia merupakan satu sumber yang berpotensi untuk pengeluaran pemangkin(catalyst) yang kemudiannya boleh digunakan sebagai pemangkin asas yang kukuh dalam pengeluaran biodiesel. Objektif kajian ini adalah untuk menghasilkan dan mencirikan pemangkin dari sisa gipsum merah dan mengkaji aktiviti pemangkin dalam esterifikasi 'Free Fatty Acid' (FFA). Penyediaan pemangkin dari gipsum merah melalui rawatan haba di dalam relau menggunakan karbon diaktifkan sebagai agen penurunan telah disiasat dalam kajian sebelum ini. Pencirian pemangkin dihasilkan dilakukan menggunakan X-Ray Diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and Field Emission Scanning Electron Microscopy (FESEM). Prestasi aktiviti pemangkin yang dihasilkan dari gipsum merah dikaji dengan pengesterifikasi asid oleik dengan etanol dalam nisbah molar 1:6. Jumlah mangkin yang berbeza digunakan, 5%, 3% dan berat 1% pemangkin asid oleik untuk mencari konversi FFA dan aktiviti pemangkin dikaji berdasarkan keputusan yang diperolehi.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS

^{o}C - Temperature

l - Length

ρ - Density

s - Time (hour)

M - Mega

g - Gram

Wt - Weight Percent

CHAPTER 1

INTRODUCTION

1.1 Background of study

The process of extraction of titanium (IV) oxide from the ilmenite ores, red gypsum is produced as a by-product. Red gypsum, a reddish brown semi-solid mud that is predominantly produced as by-product in this industry have been causing problems such as storing and environmental pollution. The total accumulation of red gypsum in Malaysia is at least 340,000 tons per year. The major composition of red gypsum are $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3.

The search for alternatives to energy source basically for petroleum-based fuel has led to the development of biofuels from various sources, including renewable feedstock likely fats and oils. This ‘biofuels’ term refers to liquid, gas and solid fuels predominantly produced from biomass. Biofuels include biodiesel, bioethanol, biomethanol and biohydrogen. According to a study conducted by U.S Department of Energy, production and use of biodiesel, compared to petroleum diesel, resulted in a

78.5% reduction in carbon dioxide emissions. Biodiesel defined as monoalkyl ester of vegetable oils or animal fats. It is an attractive alternative fuel because it is environmental friendly and can be synthesized from edible and non-edible oils. Biodiesel is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst.

Many researches have been carried out on biodiesel production using different oils as the raw material, different alcohols and different catalyst. Recent research has focused on the application of heterogeneous catalysts to produce biodiesel, because of their environmental and economic advantages compared to homogeneous catalysts which cannot be reused and requires tedious washing and separating steps. To date, many solid base catalysts have been developed for biodiesel production, such as basic zeolites, alkaline earth metal oxides and hydrotalcites. Among all the solid base catalysts, calcium oxide, CaO have attracted much attention due to their relatively high basic strength, low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide.

Investigation of the reductive decomposition of $CaSO_4$ with H_2, C, and CO has been undertaken to generate SO_2 for the production of sulfuric acid as well as the regeneration of lime from sulfated absorbent. However, it was found that the unfavorable product CaS and CaO were formed during the reductive decomposition of $CaSO_4$. Further investigation on reductive decomposition of $CaSO_4$ was carried out under a CO—CO_2 atmosphere and was found proportion of CaO in the products increased as the concentration ratio of CO/CO_2 decreased. Thermal reduction study illustrates that gypsum can be reduced to calcium sulphide, CaS with reducing agents like activated carbon in a tube furnace operating at 1100 ^oC. The study showed the

addition of carbon to gypsum at 1:1 moles ratio showed that only 13 % of gypsum was converted to CaS while CaO conversion of 38 % is obtained. The percentage conversion results further explain that CaO formation is favored by a carbon ratio used. Red gypsum which mainly contains $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3 is a potential source for catalyst production which later can be used as solid base catalysts in biodiesel production.

1.2 Problem Statement

Red gypsum is a waste product of local industry in Malaysia which is formed during the extraction of titanium (IV) oxide from the ilmenite ores and they are accumulating in landfill and polluting the environment. This Accumulation in landfill and emission of harmful gas such as hydrogen sulfide, H_2S (Satoshi Okumura, et. al., 2003). These concerns have increased the effort to find an end use for the red gypsum industrial waste. At the same time there is a crucial need to find an alternative fuel in fulfilling energy demand to replace fossil fuels which are undergoing drastic depletion. The best option is biodiesel which shows almost same properties like fossil fuels and most importantly it is environmental friendly. Red gypsum which mainly contains $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3 is a potential source for catalyst production which later can be used as catalyst in biodiesel production.

1.3 Research objectives

To produce and characterize catalyst from local industry waste, red gypsum for biodiesel synthesis

1.4 Scopes of study

For the purpose of achieving the objective, the scopes of studies are stated as below:

I. Study the ways to synthesize catalyst from red gypsum ($CaSO_4.2H_2O$)

II. Choose the best method to prepare catalyst from red gypsum ($CaSO_4.2H_2O$).

III. To characterize the catalyst prepared from red gypsum ($CaSO_4.2H_2O$).

IV. To study the activity of the catalyst prepared by esterification of Free Fatty Acid (FFA) produced from oil.

1.5 Rationale and significance of study

The rationale of this research is to provide empirical evidence that catalyst can be produced or prepared from waste Red Gypsum. The result of this research would signify the performance and efficiency of the catalyst produced in biodiesel synthesis. The identification of this process of preparing catalyst from red gypsum will be one of the steps to reduce the environmental issue cause by this waste.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

There is a crucial need to find end uses for the industrial waste of local industry, red gypsum which is formed during the extraction of titanium (IV) oxide from the ilmenite ores. Red gypsum which mainly contains $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3 is a potential source for catalyst production which later can be used as solid base catalysts in biodiesel production. This chapter of literature review comprises of three major themes discussing on red gypsum and reductive decomposition of red gypsum to catalyst, biodiesel and catalyst in biodiesel production.

2.2 Red Gypsum

Many studies have been carried out to find proper end uses for red gypsum which causes problems such as storing and environmental pollution. I. Fauziah, et. al., 1996, investigated on land application of red gypsum because of its potential use as a soil amendment in Malaysia. According to them, red gypsum, a reddish brown semi solid mud, is a waste product from an industrial process which extracts titanium (IV) oxide from the ilmenite ores and it is commonly known as 'red' gypsum because of the iron content of ilmenite. They further explain on the extraction of titanium (IV) oxide from ilmenite by digestion of sulphuric acid and neutralization of the spent acid produces waste product gypsum.

In 2007, Rose Aini Kamarudin and Mohd. Shahir Zakaria carried out a research to utilize the red gypsum in production of glaze. They found out that the total accumulation of red gypsum in Malaysia is at least 340,000 tons per year after having personal communications with the local industry. Their examination on red gypsum waste composition revealed that it major composition are $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3 which can form a glassy phase after sintering. It was found that the addition of up to 36 % of the RG waste was possible in the production of glazes.

2.2.1 Reductive Decomposition of Red Gypsum to Calcium Oxide, CaO

Waste gypsum has been a major problem as it is causing storage issue due to the shortage of landfill sites. In order to achieve a sustainable and greening the environment, recycling and utilization of Ca-based solid waste is considered as a promising undertaking in proper management of waste gypsum. Investigations on reductive decomposition of $CaSO_4$ in CO atmosphere have been actively conducted by many researches in this several decades. Hull et et al., 1957, investigated the reductive decompostion of CaSO4 depended on the reaction temperature as well as CO and CO2 concentrations. Wheelock et al., 1960, Gruncharov et al., 1985, and Kuusik et al., 1985, found that the proportion of CaO in the products increased as the concentration ratio of CO/CO2 decreased in their respectives study on for the reductive decomposition of CaSO4 in a CO-CO2 atmosphere. In addition Wheelock et al., 1986 stated that CaO and CaS generated by CaSO4 decomposition via Equation (2.1) and (2.2),

$$CaSO_4 + CO \longrightarrow CaO + SO_2 + CO_2 \quad (2.1)$$

$$CaSO_4 + 4CO \longrightarrow CaS + 4CO_2 \quad (2.2)$$

Gruncharov et al., 1985, further reported on the strong effects of admixtures of Fe_2O_3, SiO_2 and $Al2O_3$ on the kinetics decomposition of $CaSO_4$. Meanwhile, Chen and Yang, 1979, stated that there are two consecutive steps in the regeneration of CaO from $CaSO_4$ proceeded through equation (2) and (3). They added that the reaction of $CaSO_4$ with CaS expressed by equation (2.3) was the rate-determining step at relatively low

temperatures. Years after, Oh JS and Wheelock TD (1990) further explain a two-step mechanism of $CaSO_4$ decomposition by proposing equation (2.4) and (2.5) assuming the presence of intermediate product $CaSO_3$.

$$CaS + 3CaSO4 \longrightarrow 4CaO+ 4SO2 \quad (2.3)$$

$$CaSO4 + CO \longrightarrow CaSO3 + CO2 \quad (2.4)$$

$$CaSO3 \longrightarrow CaO + SO2 \quad (2.5)$$

In 2003, Satoshi Okumura et al., studied the recovery of CaO by reductive decomposition of spent gypsum in a $CO\text{-}CO_2\text{-}N_2$ atmosphere. This study was crucial as large amount of waste gypsum were discarded in Japan causing environmental problem due to the emission of harmful gas such as H_2S from waste gypsum from landfill sites. Initially, the investigation on the reductive decomposition of $CaSO_4$ with H_2, C, and CO is to generate SO_2 for the production of sulfuric acid and to generate lime from the sulfated absorbent. Satoshi Okumura et al., (2003), used a packed-bed reactor to regenerate an alternative CaO sorbent. Various process conditions were used to operate the reactor including an increasing CO concentration, CO/CO_2 concentration ratio (0.067-1), and temperature (1123- 1273 K) which in all cases N_2 was used as a balancing gas. The $CO\text{-}CO_2\text{-}N_2$ atmosphere found to be most effective for the regeneration of CaO from $CaSO_4$ and influenced by the CO/CO2 concentration ratio. On the other hand, in a $CO\text{-}N_2$ atmosphere, CaS was predominantly produced confirming Wheelock et al., 1960, stated that the ratio of unfavorable product CaS to CaO depended on the reaction

temperature as well as CO and CO2 concentrations. They added that, the SO_2 absorption capacity of CaO regenerated from CaSO4 was higher than that of limestone-calcined CaO and larger pore diameter of the regenerated CaO was considered to be responsible for the higher SO_2 absorptivity. Satoshi Okumura et al., 2003, pointed out several equations to illustrate the reactions of the reductive decomposition of $CaSO_4$ with CO.

$$CaSO_4 + CO \longrightarrow CaO + SO_2 + CO_2 \quad (2.6)$$

$$CaSO_4 + 4CO \longrightarrow CaS + 4CO_2 \quad (2.7)$$

$$CaSO_4 \longrightarrow CaO + SO_3 \quad (2.8)$$

$$CaS + 3SO_3 \longrightarrow CaO + 4SO_2 \quad (2.9)$$

$$CaSO_4 \longrightarrow CaO + SO_2 + 1/2O_2 \quad (2.10)$$

$$CaSO_4 + 1/3CaS \longrightarrow 4/3CaO + 4/3SO_2 \quad (2.11)$$

$$CaSO4 + CO \longrightarrow CaSO_3 + CO_2 \quad (2.12)$$

$$CaSO_3 \longrightarrow CaO + SO_2 \quad (2.13)$$

2.2.2 Reductive Decomposition of Red Gypsum to Calcium Sulphide, CaS

In 2009 *N.R. Mbhele* et al., done a research in a respond to gypsum waste disposal sites which are the main reason for the leaching of saline water into surface and underground water and create airborne dust. They mentioned gypsum waste is not only an environmental problem but has measurable economic value in which valuable/saleable byproducts like sulphur and calcium carbonate be recovered from the low quality gypsum. A research in the process for converting waste gypsum into sulphur is done in which the process evaluated consists of the following stages: reduction of gypsum to calcium sulphide; stripping of the sulphide with CO_2 gas and the production of sulphur. Thermal reduction study showed that gypsum can be reduced to calcium sulphide, CaS with activated carbon in a tube furnace operating at 1100 ºC. Their studies shows that reducing agents like coal and activated carbon can be used to reduce gypsum to CaS in a furnace. Based on the study we know that the addition of carbon to gypsum at 1:1 moles ratio showed that only 13 % of gypsum was converted to CaS while CaO conversion of 38 % is obtained. The percentage conversion results further showed that CaO formation is favoured by a carbon. In another research Hongjing Tian et al., 2010, shows that the mole fraction of CaS is higher than CaO when the reacting temperature is below 1000 °C and that the direct reductive products after the reduction of $CaSO_4$ were merely CaO in the temperature range from 900 to 1180 °C.

2.3 Biodiesel

The search for alternatives to energy source basically for petroleum-based fuel has led to the development of biofuels from various sources, including renewable feedstock likely fats and oils. This 'biofuels' term refers to liquid, gas and solid fuels predominantly produced from biomass. Biofuels include biodiesel, bioethanol, biomethanol and biohydrogen. Biodiesel defined as monoalkyl ester of vegetable oils or animal fats. It is an attractive alternative fuel because it is environmental friendly and can be synthesized from edible and non-edible oils.

According to N.N.A.N. Yusuf, S.K. Kamarudin et al., 2010, biodiesel is the monoalkyl esters of vegetable oils or animal fats which is an attractive alternative fuel because of its environmental friendly characteristic and can be predominantly produced from both edible and non-edible oils. Biodiesel primarily produced from food crops which are mostly oil seeds (Teresa M. Mata et. al., 2009). Gui et. al., 2008 stated that 95% of the world biodiesel production is from edible oils which are easily available on large scale from the agricultural industry. This agricultural industry supplies conventionally grown edible oils such as rapeseed, soybean, sunflower and palm for biodiesel production, thus lead to food versus fuel issues (Mustafa Balat, 2010).

Teresa et al., 2009, stipulates on development of second generation biodiesel which is produced from non-edible oils is highly concerned as the first generation biodiesel, primarily produced from edible oils have limited ability to achieve targets for biodiesel production. They added, biodiesel which is produced from non-food feedstock have high potential in offering utmost opportunities in a longer term. Improper planning in continuous and large scale production of biodiesel from edible oils may have negative

impact to the world, for instance depletion of food source consequently lead to economic crisis (Gui et. al., 2008).

2.3.1 Production of biodiesel from edible oils

Previous study on biodiesel production from edble oils were done by many researchers. Among those, Rathore (2007) studied the synthesis of biodiesel from edible oils such as palm oil and groundnut oil and also from crude non-edible oils which are Pongamia pinnata and Jatropha curcas. The oils were investigated in supercritical methanol and ethanol without using any catalyst.

Biodiesel fuel (BDF) is said to be the alternative of diesel fuel with promising future. Currently, palm oil in southeastern Asia, edible oil such as soybean oil in USA and rapeseed oil in Europe has been used to produce biodiesel (Azam et al., 2005). However, the rise in both cost and demand for edible oils makes it difficult to be used in production of BDF. In addition, in numerous countries, government does not encourage research done on biodiesel production from edible oils. Therefore, waste vegetable oil, non-edible oils and animal fats such as salmon oil, beef tallow, poultry fat, and greases are seen as future promising alternative feedstocks production of biodiesel. The search for other low cost feedstock is also in demand nowadays (Guana and Kusakabe, 2012).

2.3.2 Production of biodiesel from non-edible oils

Gui et. al. (2008) production of second generation biodiesel from non-edible oils is highly concerned with high free fatty acid (FFA) content which has caused conventional transesterification reaction especially the alkaline-catalyzed process not feasible. They added that the reaction between the FFA with alkaline catalyst produces soap thus inhibit the separation of ester and glycerin. They mentioned that the best method to extract biodiesel from non-edible oils as suggested by several researchers is a two-step transesterification process.

A further explanation by them is specifically on the two steps process which starts with the initial step of reduction of the FFA content in the oil by acid-catalyzed esterification process followed by the second step where the oil and methanol is converted to methyl ester and glycerol in an alkaline-catalyzed process. Even though the disadvantage of this process is the high production cost as pointed out by Gui et. al., 2008 meanwhile Saka S., 2005, stressed on the advantage in which this two step process was found to be highly effective as the yield of biodiesel in the overall process reaching up to above 90%.

With regard to Ritesh Kumar et. al., 2011, study there are five parts in this microwave assisted transesterification process which are the chemicals, extraction of oil, microwave assisted transesterification itself, separation and purification of biodiesel, ester content and fuel properties of biodiesel. First, the chemical used in the experiment were analytical reagent grade and were used without purification and the rubber seed oil was extracted using a mechanical oil expeller which later on filtered and kept in an air tight container undisturbed for three to four days for the suspended particles to settle.

Microwave assisted transesterification carried out using two alkali catalysts namely sodium hydroxide(NaOH) and potassium hydroxide(KOH) where the reaction was timed as soon as the desired transesterification temperature (60°C) was achieved. Next the reaction was continue for few different times, suggested 3, 5, 7 and 10 minute in which for each reaction the experiment was repeated for four times and their average value was obtained. Separation and purification of biodiesel undergo few processes in which the first process is capturing the reaction by immersing the glass reactor in an ice bath and as the reaction stopped, the product was kept in separating funnel over night for separating biodiesel and glycerol. The next part was calculation of biodiesel yield relative to the initial amount rubber seed oil by weight the biodiesel purity was determined according to the relative methyl ester content obtained by gas chromatography (GC) analysis. (GC) analysis is done to determine the amounts of products (Yang et al., 2011) and using equation as below:

$$\text{Yield} = \frac{Actual\ \ amount\ \ of\ biodiesel\ (g)}{Theoretical\ \ amount\ \ of\ biodiesel\ (g)} \times 100(\%) \qquad (2.14)$$

Finally ester content and fuel properties of biodiesel were determined using ASTM (D6751) standards as shown in Table 3.2. The experimental results indicates that the transesterification of rubber seed oil can be done in 5 to 10 minutes, as compared to conventional heating where approximately 3 hours is required for the reaction. Thus use of microwave will help in considerable time and cost saving (Ritesh Kumar et. al., 2011).